Short communication

Performance improvement of gel- and solid-state dye-sensitized solar cells by utilization the blending effect of poly (vinylidene fluoride-co-hexafluropropylene) and poly (acrylonitrile-co-vinyl acetate) co-polymers

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HIGHLIGHTS

- Polymer blend electrolyte was prepared for gel- and solid-state DSSCs.
- PVDF-HFP and PAN-VA co-polymers are used as gelators.
- 75% PVDF-HFP has achieved higher conductivity than pure polymers.
- Efficiencies obtained for gel and solid-state cells are 6.3% and 4.88% respectively.
- The efficiency of the solid-state cell improved to 5.34% by TiO_2 fillers.

ARTICLE INFO

ABSTRACT

Poly (vinylidene fluoride-co-hexafluropropylene) (PVDF-HFP) and poly (acrylonitrile-co-vinyl acetate) (PAN-VA) are used as gelator to prepare gel- and solid-state polymer electrolytes for dye sensitized solar cells (DSSCs) applications. The electrolytes prepared using PVDF-HFP have higher conductivities than those prepared using PAN-VA. In blended polymers, the conductivities of the electrolytes increase with increasing composition of PVDF-HFP; at 75% PVDF-HFP, conductivity of the blended polymer surpassed that of pure polymers. It is also found that the viscosity of the electrolyte prepared by PAN-VA (1.2 kPaS) is much lower than that by PVDF-HFP (11 kPaS). Therefore, increasing PAN-VA composition can decrease the viscosity of the electrolyte, improving the penetration of electrolytes in the TiO_2 matrix. By controlling the ratio of PVDF-HFP/PAN-VA, the conductivity and viscosity of the electrolyte can be regulated and an optimal ratio based on the conversion efficiency of the gel- and solid state DSSCs is obtained at the ratio of 3/1. The highest efficiency achieved by the gel- and solid-state cells using the blending polymers are 6.3% and 4.88%, respectively, which are higher than those prepared using pure polymers (5.53% and 4.56%, respectively). The introduction of TiO_2 fillers to the solid electrolyte can further increase the cell efficiency to 5.34%.

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1. Introduction

The use of dye-sensitized solar cell (DSSCs) as a promising alternative for organic photovoltaic devices has attracted great attention because of being light weight, low production cost, and having high energy conversion efficiency [1–4]. Among various kinds of DSSCs, ruthenium complex and zinc porphyrin dyes sensitized cells have showed higher efficiencies of 11% and 12% respectively [5–7] In most instances, these cells are required acetonitrile as solvent to prepare the liquid electrolytes which affects the long-term stability of the cells due to leakage and evaporation of the solvents [8,9] As an alternative to the liquid electrolytes, solid and gel materials were used to fabricate the gel and solid-state cells where lower energy conversion efficiencies were obtained in comparison to liquid versions [10–14]. This is because of the lower charge conductivities of the gel and solid

materials, as well as their poor contacting and filling to the nano structured TiO$_2$ electrodes. Polymer gel electrolytes (PGEs) have also been found to be a suitable alternative for liquid electrolytes in terms of ionic conductivity, thermal stability and filling ability to the mesoporous TiO$_2$ electrodes [15,16] However, new ways to improve the penetration situation in TiO$_2$ matrices due to high viscosity of the gel electrolytes, as well as increases the conductivities of the electrolytes are main focal points for obtaining highly efficient DSSCs [17,18] Accordingly, polymers such as poly (vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP) and poly (acrylonitrile-co-vinyl acetate) (PAN-VA) are attractive for the preparation of highly efficient DSSCs [19–22]. Since fluorine has smaller ionic radius and high electro negativity, PVDF-HFP is known to be helpful to enhance the ionic conductivity. By using PVDF-HFP, as well as the introduction of nano fillers, energy conversion efficiency about 7.2% was obtained for gel-state cells [23–27]. Similarly, PAN-VA was used to prepare PGEs for the high performance DSSCs where in-situ gelation of the liquid electrolytes into the mesoporous TiO$_2$ matrices achieves an efficiency of 10% [28,29]. Solid-state DSSCs fabricated using solid-state polymer electrolytes have showed lower energy conversion efficiency compared to those of liquid- and gel-state versions, mainly due to high viscosity of the solid-state electrolytes. By using PAN-VA as solidification agent, as well as applying an external pressure to increase the penetration ability of the electrolytes into mesoporous TiO$_2$, an energy conversion efficiency of 8.65% was achieved [30].

It was proved that the blending of PVDF and PEO effectively improves the ionic conductivities of the electrolytes due to change in the polymer chains and crystallization phase [9]. It was also reported that blending of PVDF-HFP and ionic liquids to prepare PGEs results in an increase in the efficiency of DSSCs [23]. Considering the cells performance of those blending systems, we tried to prepare new PGEs and solid electrolytes based on the blending of PVDF-HFP and PAN-VA polymers. Furthermore, TiO$_2$ nano particles are used as a filler to improve the performance of the solid-state DSSC.

2. Experimental

2.1. Materials

Poly (acrylonitrile-*co*-vinyl acetate) (PAN-VA, VA = 92:8) was received from Tonghwa synthetic Fiber Co. Ltd. Poly (vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP, HFP = 12%), 4-tert butylpyridine (TBP, 99%) and TiO$_2$ nano-filler (< 25 nm particle size, 99.7%) were obtained from sigma-Aldrich Co. Lithium iodide (LiI, anhydrous, 98.0%) was purchased from Fluka. Acetonitrile and Iodine (I$_2$, 99%) was obtained from Riedel-de Haën.

2.2. Preparation of photoelectrode

TiO$_2$ photoelectrodes were prepared via spin coating of the TiO$_2$ suspension on the transparent conducting substrate (TCO). Typically, Fluorine-doped tin oxide (SnO$_2$:F) FTO as TCO was cleaned with the sequence of detergent solution, acetone and de-ionized water. The Degussa P25 TiO$_2$ (21–25 nm) (10 g) was stirred with deionized water at 50 °C for 2 h, and Triton X-100 (TX-100) (100 μM) and acetylacetone (AA) (200 μM) were added into the solution with constant stirring and temperature for 8 h to get TiO$_2$ suspension. Before coating the TiO$_2$ suspension on TCO substrate, a mixture of 30 μl 0.01 M Ti(i-PrO)$_4$ and 10 ml pure ethanol was coated on the TCO substrate as a single layer and dried at 50 °C for 15 min to make a chemical bonding between substrate and TiO$_2$ thin film. After that the TiO$_2$ suspension was coated on the TCO substrate for several times and dried at 50 °C for 30 min. Finally, the photoelectrode was sintered at 450 °C for 30 min to burnout all organic binders and surfactants and get the good contact between TiO$_2$ electrode and TCO. Then the photo-electrode was immersed in N719 dye solution for about 20–30 h at room temperature.

2.3. Preparation of solid and gel-state electrolytes

For the preparation of gel and solid-state electrolytes, various composition of PAN-VA and PVDF-HFP were dissolved in acetonitrile and heated first at 60 °C for 30 min with constant stirring of 300 rpm to increase the viscosity of the electrolytes. After that the temperature was slowly increased about 5 °C for every 30 min and reached 80 °C.

2.4. Cell assembly and measurements

The cell assembly consists of N719 dye doped photoelectrode, Pt metal sputtered on TCO surface as counter electrode and various composition of PVDF-HFP/PAN-VA in acetonitrile solution as electrolyte. For gel-state cell, polymer blend electrolytes are directly injected into the cell, and to prepare the solid-state cell, the cells containing electrolytes were heated under hot air stream to evaporate the liquid solvent and then put in vacuum dry oven for 30 min at 60 °C to further remove the solvent content. After assembling the DSSC, the photovoltaic performance of the cell was analyzed by solar simulator. The resistance between electrolyte/TiO$_2$ interface, Pt/electrolyte interface, resistance inside the electrolyte and electrolytes ionic conductivity were also measured in EIS analysis. The incident photon-to-current conversion efficiency (IPCE) (Enli Technology Co., Ltd. Taiwan) was also measured to analyze the light-scattering effect in the long wavelengths.

3. Result and discussion

3.1. Composition effect of PVDF-HFP and PAN-VA on the ionic conductivity of PGEs and solid-state electrolyte

Various compositions of PVDF-HFP and PAN-VA were introduced into the electrolyte as the gelator and the overall concentration of the polymer is controlled at 10 wt%. The ionic conductivities measured for the gel-electrolytes were shown in Table 1. The result shows that the conductivity of gel-electrolyte prepared using PVDF-HFP (6.6×10^{-3} S cm^{-1}) is higher than that using only PAN-VA (5.3×10^{-3} S cm^{-1}), indicating that PVDF-HFP has superior ability, than PAN-VA, in enhancing the conductivity of PGEs. This result is attributed to the smaller ionic radius and high electro negativity of fluorine in PVDF-HFP. For the PGEs prepared using both polymers, the conductivity increases with increasing concentration of PVDF-HFP. Furthermore, at the composition of 75% PVDF-HFP/25% PAN-VA, the conductivity can obtain a value of 6.78×10^{-3} S cm^{-1}, which is even higher than that prepared by

Table 1

Conductivities and photovoltaic parameters obtained from the *I–V* curves of the polymer blend gel-state DSSCs fabricated using various composition PVDF-HFP and PAN-VA. The cell performances were measured under the illumination of one sun (AM 1.5, 100 mW cm^{-2}).

PAN-VA (wt%)	PVDF-HFP (wt%)	σ ($\times 10^{-3}$ S cm^{-1})	η (%)	FF	J_{sc} (mA cm^{-2})	V_{oc} (V)
Liquid ACN	Liquid ACN	8.87	6.18	0.69	11.98	0.75
0	100	6.56	5.53	0.70	09.91	0.80
25	75	6.78	6.30	0.70	11.47	0.78
50	50	6.08	6.28	0.70	11.46	0.78
75	25	5.84	6.04	0.71	10.82	0.79
100	0	5.30	5.46	0.69	09.76	0.81

using 100% PVDF-HFP. This result demonstrates that the polymer-blending system can improve conductivity of the PGEs.

To prepare the solid-state electrolytes, the overall concentration of polymer and I_2 were controlled at 20 wt% and 0.08 M, respectively. Table 2 shows the ionic conductivities measured for the solid-state electrolytes containing various compositions of PVDF-HFP and PAN-VA. In general, the effect of polymer composition on the ionic conductivity of the solid-state electrolytes is similar to that observed for the gel-electrolytes. The solid electrolytes prepared using PVDF-HFP and PAN-VA electrolytes have ionic conductivities of 3.46×10^{-3} S cm^{-1} and 2.34×10^{-3} S cm^{-1}, respectively. PVDF-HFP also demonstrates a higher ability, than PAN-VA, to enhance the ion conductivity of solid-electrolyte. For the blending system, the ionic conductivity of the electrolytes is proportional to the composition of PVDF-HFP, and the conductivity obtained by the 75% PVDF-HFP (3.67×10^{-3} S cm^{-1}) blending system can achieved a value higher than that prepared by pure PVDF-HFP. The above results clearly suggest that the polymer blend-system is capable of improving ionic conductivities of both PGEs and solid-state electrolytes. The decrease in the crystallinity of the polymers in the blending system is inferred to be a major factor resulting in an ionic conductivity higher than those of electrolytes prepared by using only one polymer.

3.2. Effect of PVDF-HFP/PAN-VA composition on the photovoltaic performance of gel- and solid-state DSSCs

Fig. 1 shows the $I-V$ curves measured for both gel-state and solid-state DSSCs fabricated using various compositions of PVDF-HFP and PAN-VA. The corresponding open-circuit potential (V_{oc}), short-circuit current density (J_{sc}), fill factor (FF) and overall energy conversion efficiency (η) of these cells are summarized in Tables 1 and 2 The overall conversion efficiencies of gel-state DSSCs prepared using PVDF-HFP and PAN-VA are, respectively, 5.53% and 5.46%. Although the PGE prepared by PVDF-HFP has a conductivity higher than that prepared by PAN-VA PGE, the performances of gel-state DSSCs using the two PGEs are quite close, indicating that other factor may be involved in determining the performance of the DSSCs. One important factor affecting the penetration of gel-electrolytes in the mesoporous TiO_2 matrix is the viscosity of the electrolytes. One advantage for the PAN-VA PGE is its lower viscosity (1.2 kPaS) compared to that of the PVDF-HFP PGE (11 kPaS), which is inferred to be the reason leading to the similar efficiencies of the two gel-state DSSCs.

For the gel-state DSSCs prepared using blending polymers, it is interesting to find that all these cells have efficiencies higher than those prepared using only PVDF-HFP or PAN-VA. When 25% of PVDF-HFP was introduced into the PGE, the overall conversion efficiency of the cell increases from 5.46% (for pure PAN-VA) to 6.04%. The efficiency can further be increased to 6.28% when PVDF-HFP composition is elevated to 50%. However, increasing the PVDF-HFP composition to 75% cannot significantly increase the performance of the cell although the corresponding PGE has the highest ionic conductivity among the studied systems. The contrary results
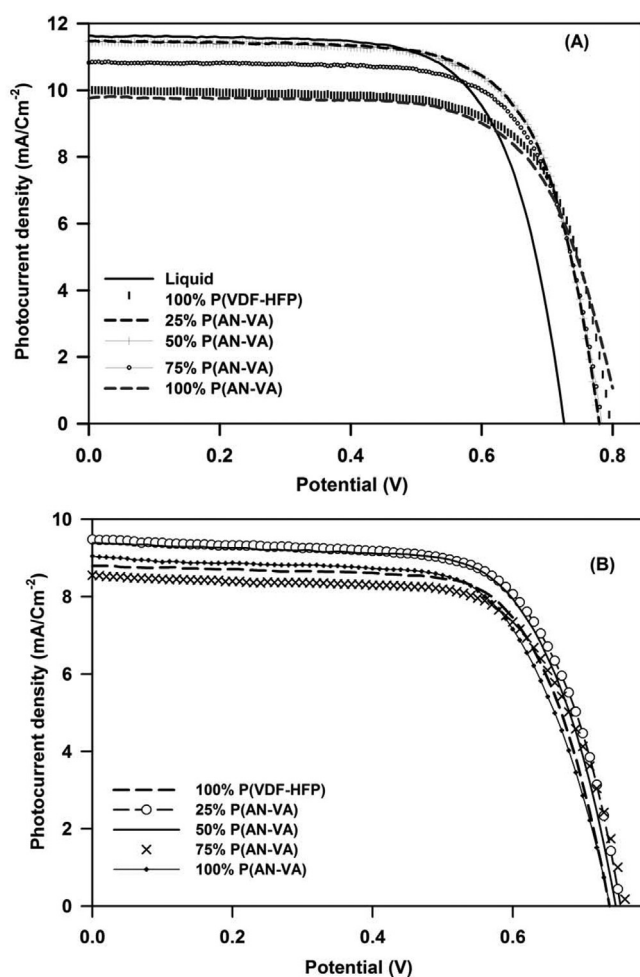

Fig. 1. $I-V$ characteristics of (A) gel-state and (B) solid-state dye sensitized solar cells fabricated using polymer blend electrolytes containing various compositions of PAN-VA and PVDF-HFP. The measurement was performed under the illumination of one sun (AM 1.5, 100 mW cm^{-2}).

between ionic conductivity of the PGEs and the efficiencies of the DSSCs can also ascribed to the viscosity effect of the electrolytes on the cell performance. As described previously, the PAN-VA PGE has lower viscosity compared to that of PVDF-HFP PGE. Therefore, although increasing the PVDF-HFP composition in PGEs will increase the ionic conductivity, it also increases the viscosity of PGE, which is disadvantageous to the penetration of an electrolyte in the TiO_2 film. That is why the two cells using 50% and 75% PVDF-HFP PGEs have nearly identical efficiencies. The higher efficiencies obtained for the gel-state DSSCs using blending polymers, in comparison with that using single polymer, indicates that it is capable of increasing the cell performance by regulating the conductivity and viscosity of electrolytes through the utilization of blending polymers.

Table 2
Conductivities, photovoltaic parameters and resistances obtained from the $I-V$ curves of the solid-state DSSC fabricated using various compositions of PAN-VA and PVDF-HFP. The cell performances were measured under the illumination of one sun (AM 1.5, 100 mW cm^{-2}).

PAN-VA (wt%)	PVDF-HFP (wt%)	σ (10^{-3} S cm^{-1})	η (%)	FF	J_{sc} (mA cm^{-2})	V_{oc} (V)	R_{pt} (Ωcm^2)	R_{TiO_2} (Ω)
0	100	3.46	4.56	0.70	8.79	0.74	6.6	41.1
25	75	3.67	4.88	0.68	9.48	0.75	6.4	45.6
50	50	3.19	4.83	0.69	9.38	0.75	6.6	44.1
75	25	2.58	4.44	0.68	8.55	0.76	7.9	48.0
100	0	2.34	4.48	0.67	9.05	0.74	8.1	49.3

It is interesting to note that, although the conductivity of the gel-electrolyte is lower than that of the liquid one, the efficiency of the gel-state cell contains the best polymer blend electrolyte is slightly higher than that of liquid state cell. It has been shown in a previous work [31] that conductivity is not the only factor determining the performance of DSSCs. Penetration of electrolyte is also very important. The result here implies that the gel-electrolyte can penetrate as well as the liquid electrolyte and, meanwhile, the conductivity is high enough to operate this photoelectrode. One important factor leading to the higher performance of the gel-state cell is its higher V_{OC}, in comparison to the liquid one. It indicates that the presence of gelators can elevator the V_{oc} value which also contributes to the higher performance of the gel-state cell.

For solid-state DSSCs, overall efficiencies of 4.56% and 4.48% are measured for PVDF-HFP and PAN-VA, respectively, and the highest efficiency (ca. 4.8%) appears at the cell prepared by 50% or 75% PVDF-HFP. Also, the cell efficiency measured for the blending system can achieve a value higher than that for the pure polymer. It is noteworthy that the blending effect of PVDF-HFP and PAN-VA on the performance of solid-state cells is similar to its effect on the gel-state cells. This result implies that the performance of the solid-state DSSCs is also controlled both by the conductivity and the viscosity of the electrolytes.

3.3. Electrochemical impedance analysis of both PGEs and solid-state electrolytes

Electrochemical impedance spectra (EIS) were measured to elucidate the charge-transport behavior in the solid-state DSSCs. The Nequest plots of the EIS spectra (Fig. 2) include three semicircles. They correspond, from left to right, respectively, to charge transfer resistance at the Pt counter electrode (R_{pt}), the reaction at the TiO$_2$/dye/electrolyte interface (R_{TiO_2}), and the diffusion of I_3^- in the electrolyte (RD). The charge transfer resistances at the Pt/electrolyte (R_{pt}) and photoelectrode/electrolyte (R_{TiO_2}), obtained by fitting the EIS spectra with an equivalent circuit shown in the insect, were listed in Table 2. For solid-state cells using pure PAN-VA and pure PVDF-HFP, the values of R_{pt} are 8.1 and 6.6 Ωcm^2 respectively. The lower R_{pt} measured for the PVDF-HFP indicates a higher electro-activity at the electrolyte/Pt interface, which is attributed to the higher ionic conductivity of the PVDF-HFP electrolyte. This inference is sustained by the similar R_{pt} values

measured for the electrolytes prepared by 50% and 75% PVDF-HFP. For the electrolyte prepared by 25% PVDF-HFP, the lower conductivity is responsible to its relatively higher R_{pt} value.

The values of R_{TiO_2} for the cells preparing by PAN-VA and PVDF-HFP electrolytes are 49.3 and 41 Ω, respectively. The lower R_{TiO_2} value measured for the PVDF-HFP electrolyte implies a more significant charge-recombination event in the corresponding cell, which is contrary to its higher conductivity. Therefore, electrolyte penetration state in the TiO$_2$ film should be responsible to this result. As discussed previously, the higher viscosity of PVDF-HFP electrolyte will trigger a less penetration state of the electrolyte and, therefore, the charge recombination is more significant. This is why the PVDF-HFP electrolyte has higher conductivity, but similar cell conversion efficiency compared to that of PAN-VA system. For the blending systems, the R_{TiO_2} value increases when PAN-VA is introduced into the electrolyte, attributable to the improvement in the electrolyte penetration. The higher R_{TiO_2} values measured for the 75% and 50% PVDF-HFP systems are consistent with their higher conversion efficiency. For the 25% PVDF-HFP system, although the R_{TiO_2} value is high, the higher R_{pt} value limits the performance of this cell.

3.4. Effect of TiO$_2$ fillers on the electrolyte conductivity and performance of solid-state DSSCs

Since TiO$_2$ had been proved to be able to increase the performance of solid-state DSSCs, this strategy is used for the optimal blending system, 25% PAN-VA/75% PVDF-HFP, in this work. Various concentrations of TiO$_2$ fillers were introduced into the electrolytes and ionic conductivities measured for the solid-state electrolytes were shown in Table 3. The result shows that the conductivity increases with increasing concentration of TiO$_2$ filler, approaches the maximum value of 4.38×10^{-3} S cm^{-1} at 7 wt% TiO$_2$. Increase of filler concentration to 10 wt% cannot further improve the conductivity. The $I-V$ characteristics of the corresponding solid-state DSSCs are shown in Fig. 3 and the related parameters were list in Table 3. It shows that the overall efficiency of the cell increases slightly when 3 wt% TiO$_2$ filler is introduced. The efficiency of the cell increases to 5.32 and 5.34%, respectively, when 5 and 7 wt% of TiO$_2$ were added in the electrolyte. Further increasing the percentage of the TiO$_2$ to 10 wt% will slightly decreases the efficiency of the cell.

3.5. Incident photon-to-current conversion efficiency

Fig. 4 shows the IPCE spectra of DSSCs with different electrolytes in the wavelength region 300—800 nm. The optimal PAN-VA/PVDF ratio (1/3) is used for the preparation of gel- and solid electrolytes. Since the same dye (N719) was used for these cells, all the cells have the same absorbance range in these IPCE spectra. However, the liquid cell demonstrates the highest IPCE values among them, and a value about 72% is obtained at a wavelength of 540 nm. For a gel-
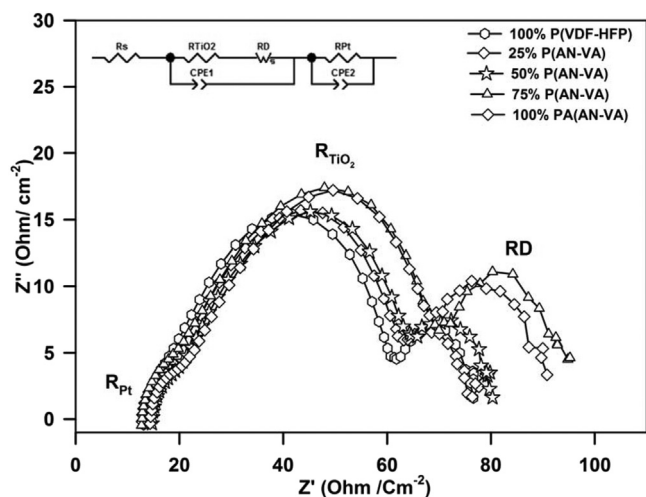

Fig. 2. Nyquist plots of the EIS spectra measured for the solid-state DSSCs fabricated using polymer blend electrolytes containing various compositions of PAN-VA and PVDF-HFP.

Table 3
Conductivities and photovoltaic parameters obtained from the $I-V$ curves of the solid-state DSSCs prepared using 25% PAN-VA electrolytes and various percentages of TiO$_2$. The cell performances were measured under the illumination of one sun (AM 1.5, 100 mW cm^{-2}).

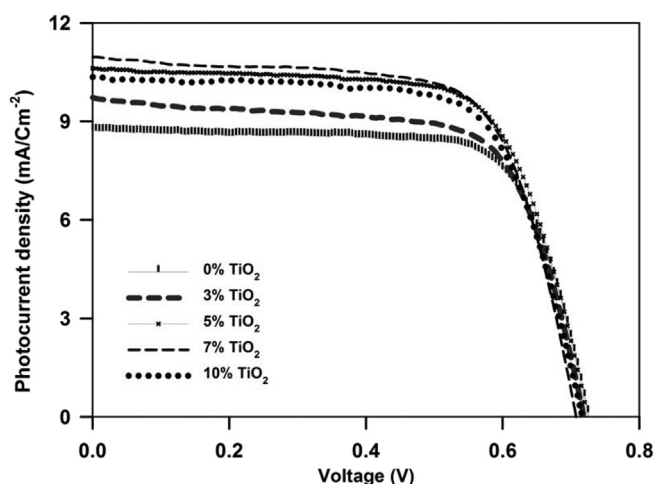| TiO$_2$ (wt%)	σ ($\times 10^{-3}$ S cm^{-1})	η (%)	FF	J_{sc} (mA cm^{-2})	V_{oc} (V)
0	3.67	4.88	0.72	8.73	0.73
3	3.75	4.98	0.68	9.72	0.72
5	3.85	5.32	0.69	10.61	0.72
7	4.38	5.34	0.69	10.96	0.71
10	4.34	5.15	0.70	10.35	0.71

Fig. 3. *I–V* characteristics of DSSCs fabricated using 25% PAN-VA based solid-state electrolytes containing various concentration of TiO_2.
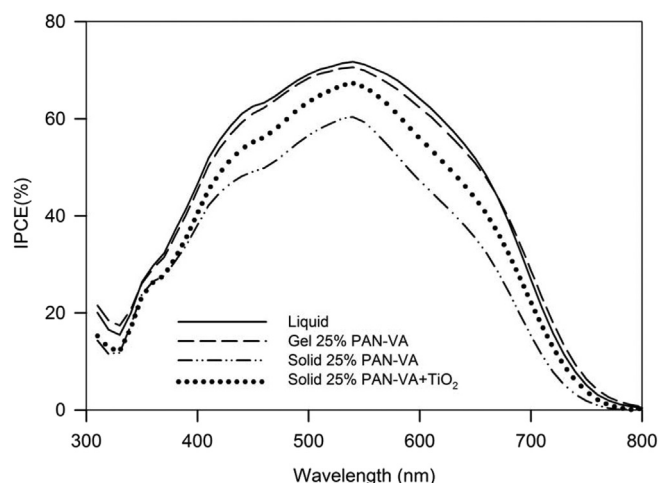

Fig. 4. IPCE spectra of DSSCs fabricated using liquid electrolytes, 25% PAN-VA based gel- and solid-state electrolytes.

state cell, the IPCE spectrum is very close to that of the liquid cell which is consistent with the similar J_{sc} values of the two cells. For the solid-state cells, the IPCE decreases a lot due to reduced ionic conductivity of the solid electrolyte. The IPCE of the solid-state cell increases to 67.38% when 10 wt% TiO_2 filler was introduced into the electrolyte. The increase in the efficiency is attributed to the light scattering and conductivity of the nano fillers.

4. Conclusion

The gel and solid-state polymer electrolytes have been prepared by using the blending of PAN-VA and PVDF-HFP polymers to improve the performance of the gel and solid state DSSCs. In preparing the gel and solid-state electrolytes, increasing the composition of PVDF-HFP significantly increases the conductivities of the electrolytes, and higher conductivity than that of pure polymers was achieved at 75% PVDF-HFP. However, the efficiencies of the cells are not significantly affected by the conductivity increases, but are dependent on the penetration of the electrolytes in the TiO_2 matrix. The penetration of the electrolytes can be improved by

increasing the composition of PAN-VA, which decreases the viscosity of the blending polymer electrolytes. By using the PVDF-HFP/PAN-VA ratio 3/1, the gel and solid-state DSSCs can achieve the highest conversion efficiencies of 6.3% and 4.88%, respectively. Moreover, the introduction of TiO_2 nano particles into the solid-state electrolyte as filler can further increase the efficiency of the solid-state cells to 5.34%.

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